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Thermodynamic properties of unsaturated vapour and liquid states from a cubic equation of state: supercritical and compressed liquid regions

P.C.N. Mak and J. Lielmezs [1]

Chemical Engineering Department, The University of British Columbia, Vancouver, BC (Canada)

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Abstract

The applicability of the Lielmezs–Merriman (LM) modification of the Peng–Robinson equation of state has been tested for supercritical and compressed liquid regions. The predicted thermodynamic properties (pressure, volume, temperature, departure functions: ΔH, ΔA, ΔS, ΔG, ΔU) and fugacity of the pure compounds have been compared with experimental data and with results calculated by the Soave–Redlich–Kwong (SRK) and Peng–Robinson (PR) equations of state.

LIST OF SYMBOLS

A	molar Helmholtz free energy
AAD	average absolute deviation
f	fugacity
G	molar Gibbs free energy
H	enthalpy
N	number of data points
NC	number of compounds
P	pressure
RMS	root mean square
S	molar entropy
T	absolute temperature
U	molar internal energy
V	volume
Z	compressibility factor

Greek symbols

α	temperature dependence of the parameter a in the cubic equation of state; see Lielmezs and Mak [1]

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[1] Author to whom correspondence should be addressed.

Subscripts

r reduced property

Superscripts

$^{\circ}$ reference state; ideal gas state

INTRODUCTION

Recently, Lielmezs and Mak [1] by means of a generalized L–H–C-type [2] temperature function, extended the work of Lielmezs and Merriman [3] over the saturated and subcritical regions of a P–V–T surface (Fig. 1). We now further explore Lielmezs and Mak's study [1] to include testing over the supercritical and compressed liquid regions. The thermodynamic properties tested for these two regions are pressure, volume, temperature, the departure functions (ΔH, ΔA, ΔS, ΔG, ΔU) and the fugacity, see Tables 1–3 and Figs. 2–7.

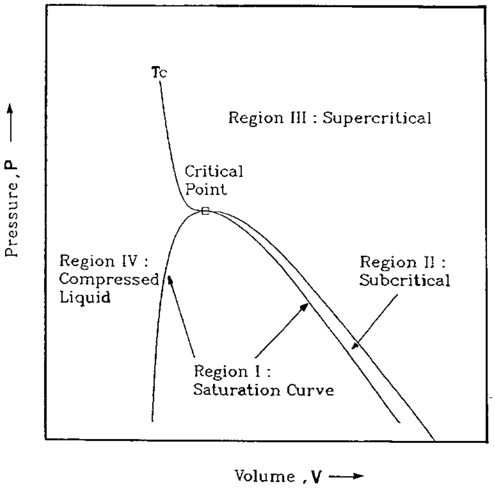

Fig. 1. Division of pressure–volume surface.

The results for a series of pure substances obtained here have been compared with those from the Soave–Redlich–Kwong (SRK) equation [14–16] and the Peng–Robinson [17] equation of state by means of RMS % error and AAD values, see Tables 2a, 2b, 3a, 3b and Figs. 2–7. RMS % error is defined as

$$\text{RMS \% error} = \left[\frac{\Sigma(\% \text{ error})^2}{N} \right]^{1/2}$$

TABLE 1

Summary of data and curve-fitted constants p, q used [a]

Compound	MW	P_c (atm)	T_c (K)	T_b (K)	ω	p	q
Methane	16.042	45.80	190.65	111.70	0.008	0.19584	0.78426
Ethane	30.068	48.20	305.42	184.47	0.098	0.25183	0.83742
Propane	44.094	42.01	369.96	231.10	0.152	0.27413	0.85176
n-Butane	58.123	37.47	425.16	272.67	0.193	0.28984	0.87067
i-Butane	58.123	36.00	408.13	261.32	0.176	0.27968	0.87124
n-Pentane	72.1498	33.25	469.65	309.19	0.251	0.30395	0.86468
i-Pentane	72.1498	33.37	460.39	301.025	0.227	0.29387	0.85979
Neopentane	72.1498	31.54	433.75	282.628	0.197	0.27709	0.87028
n-Hexane	86.170	29.91	507.87	341.87	0.296	0.30876	0.81677
n-Heptane	100.205	27.00	540.20	371.60	0.351	0.32020	0.82035
n-Octane	114.232	24.50	568.80	398.80	0.394	0.32632	0.81321
Benzene	78.108	48.70	562.65	353.25	0.212	0.30668	0.82281
Sulphur dioxide	64.066	77.79	430.65	263.00	0.251	0.36256	0.83570
Methanol	32.042	78.59	513.15	337.696	0.559	0.47075	0.80070
Ethanol	46.069	60.56	513.92	351.443	0.6436	0.47769	0.84658
1-Propanol	60.090	50.21	537.04	370.93	0.624	0.45585	0.91571
Acetylene	26.036	61.64	308.69	189.20	0.184	0.30632	0.80464
Propylene	42.078	45.60	364.91	225.45	0.148	0.27311	0.83694
1-Butene	56.104	39.67	419.59	266.90	0.187	0.29085	0.85773
Water	18.0152	218.3	647.30	373.15	0.344	0.44221	0.73237
Nitrogen	28.016	33.49	125.95	77.40	0.040	0.20477	0.81713
Ammonia	17.032	111.3	405.59	239.70	0.250	0.38595	0.85842
Neon	20.179	26.19	44.40	27.09	0.000	0.14466	0.76353
Argon	39.944	48.33	150.86	87.29	−0.004	0.18893	0.78649

[a] Physical properties that are not given in the original data source are taken from reference 4. Equations of state needed for calculations are given by Lielmezs and Mak [1].

$$\% \text{ error} = \frac{\text{Experimental} - \text{Calculated}}{\text{Experimental}} \times 100$$

and AAD is defined as

$$\text{AAD} = \frac{|\text{Deviation}|}{N}$$

where Deviation = Experimental − Calculated and N = number of data points.

APPLICATION OF THE PROPOSED METHOD

The relations needed to calculate thermodynamic properties for this work over the supercritical and compressed regions of the P–V–T surface (Fig. 1) have already been derived by Lielmezs and Mak [1]. Following that work [1], the saturated state temperature at 1 atm for carbon dioxide and acetylene has been taken as their "normal" boiling point temperature. The

TABLE 2a

Comparison of prediction errors: Region III—supercritical

Compound	RMS % error									T_r range	P_r range	N	Ref. [a]
	P			T			V						
	SRK	PR	LM	SRK	PR	LM	SRK	PR	LM				
Methane	4.555	13.59	13.79	1.514	7.484	7.846	2.189	4.692	4.950	1.007–7.343	0.022–21.83	272	5
Ethane	19.68	11.14	11.30	2.689	3.508	3.776	7.583	5.013	5.266	1.002–1.768	0.021–10.37	108	6
Propane	18.15	14.99	15.11	2.657	5.666	5.923	6.422	4.687	4.938	1.000–1.892	0.024–16.66	180	5
n-Butane	32.10	15.85	15.98	3.754	5.740	6.131	9.791	5.439	6.057	1.002–1.411	0.027–18.68	69	7
i-Butane	17.51	11.18	11.25	2.626	3.415	3.555	6.377	3.775	3.989	1.005–1.715	0.028–11.11	165	5
n-Pentane	23.81	24.21	24.27	3.672	10.44	10.71	8.977	7.627	7.947	1.001–1.491	0.030–21.05	144	5
i-Pentane	21.35	7.537	7.681	3.700	1.724	1.723	8.896	4.382	4.794	1.021–1.738	0.030–8.990	160	5
Neopentane	15.68	12.54	12.66	2.169	4.064	4.246	6.121	4.332	4.694	1.014–1.614	0.032–11.10	153	5
n-Hexane	10.90	4.266	4.720	1.310	0.615	1.450	5.853	2.951	3.687	1.006–1.159	0.033–1.365	174	8
n-Heptane	26.25	6.374	6.871	6.080	1.709	1.664	8.112	3.903	4.332	1.037–1.851	0.037–18.28	156	5
n-Octane	40.13	10.92	11.92	7.882	2.360	3.312	10.25	5.542	6.491	1.020–1.758	0.041–20.14	143	5
Benzene	9.189	3.199	3.684	1.397	0.581	0.597	5.155	2.515	3.082	1.031–1.777	0.021–2.027	132	5
Carbon dioxide	7.425	1.768	2.324	1.949	1.157	1.638	3.104	1.468	2.003	1.022–4.492	0.014–2.804	120	8
Sulphur dioxide	24.58	6.104	6.954	2.931	1.029	1.221	7.971	3.476	4.238	1.019–1.212	0.013–3.936	180	8
Methanol	75.74	31.61	32.74	6.258	3.774	8.754	11.17	7.620	8.186	1.013–1.949	0.013–6.907	208	5
Ethanol	44.94	17.42	18.53	5.745	3.211	7.505	9.884	6.122	6.954	1.012–1.946	0.017–8.147	182	5
1-Propanol	34.04	12.79	13.31	5.735	3.044	4.001	9.300	5.480	6.055	1.043–1.862	0.020–9.878	169	5
Acetylene	68.11	30.97	32.43	3.937	2.075	5.491	16.60	10.63	12.34	1.001–1.034	0.016–1.435	63	8
Propylene	8.498	2.601	2.714	1.455	0.683	0.787	3.565	1.574	1.902	1.020–3.745	0.022–4.476	130	8
1-Butene	10.68	3.778	3.788	3.010	1.315	1.358	4.421	1.664	1.666	1.049–2.383	0.025–12.44	195	5
Water	3.418	1.966	2.521	1.169	0.689	0.644	3.651	2.385	3.213	1.038–1.768	0.005–1.714	194	8
Ammonia	32.90	14.77	15.07	3.066	1.720	2.844	8.616	5.359	5.384	1.041–1.452	0.009–3.056	120	8
Average	24.98	11.80	12.26	3.40	3.00	3.87	7.45	4.57	5.10	Total number of data points = 3417			

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[a] P–V–T, departure function and fugacity coefficient data are taken from the same source.

TABLE 2b

Comparison of prediction errors: Region III—supercritical

Compound	Average absolute deviation (AAD)											
	ΔH (cal mol^{-1})			ΔS (cal mol^{-1} K^{-1})			ΔA (cal mol^{-1})			ΔG (cal mol^{-1})		
	SRK	PR	LM	SRK	PR	LM	SRK	PR	LM	SRK	PR	LM
Methane	16.5	31.4	39.3	0.045	0.035	0.082	12.4	8.6	10.4	9.7	29.7	32.3
Ethane	44.2	59.5	73.7	0.134	0.155	0.197	12.6	11.7	11.7	18.7	18.9	22.5
Propane	51.5	74.6	173.6	0.132	0.152	0.403	25.9	16.5	15.6	42.2	30.0	35.4
n-Butane	79.4	83.4	179.5	0.177	0.188	0.379	29.2	22.1	21.8	48.6	28.3	30.8
i-Butane	66.0	77.3	99.0	0.133	0.164	0.211	19.6	16.0	15.9	34.1	27.2	29.9
n-Pentane	189.8	192.3	298.5	0.369	0.342	0.582	51.5	35.1	35.0	58.2	46.8	50.4
i-Pentane	108.6	80.2	90.2	0.173	0.160	0.180	20.9	21.6	22.9	48.0	15.6	18.5
Neopentane	61.8	57.4	81.9	0.109	0.121	0.183	21.2	18.1	18.4	28.3	36.3	40.3
n-Hexane	231.1	217.7	201.2	0.313	0.316	0.277	99.0	96.7	95.0	118.4	99.1	101.3
n-Heptane	70.7	98.3	91.8	0.179	0.168	0.156	32.5	26.4	26.5	83.2	33.8	32.9
n-Octane	90.0	123.4	129.7	0.229	0.214	0.229	40.7	34.5	35.3	102.8	47.3	47.3
Benzene	21.8	42.4	42.5	0.039	0.047	0.047	9.1	12.5	12.6	11.8	11.1	12.2
Carbon dioxide	57.2	70.1	78.9	0.091	0.093	0.106	58.8	59.0	59.0	56.2	58.9	62.0
Sulphur dioxide	112.1	113.4	115.1	0.140	0.159	0.196	95.1	93.1	94.6	102.0	102.1	102.9
Methanol	58.6	79.3	88.7	0.124	0.124	0.140	13.0	18.1	16.7	35.4	23.1	24.7
Ethanol	66.8	78.7	110.2	0.144	0.143	0.202	11.1	11.2	12.0	52.1	31.4	39.9
1-Propanol	79.9	98.6	141.4	0.175	0.171	0.231	13.6	13.3	14.6	61.6	35.1	44.4
Acetylene	98.4	89.6	60.1	0.169	0.182	0.130	33.3	30.0	28.9	55.3	40.4	42.7
Propylene	33.7	33.5	43.3	0.060	0.060	0.069	31.1	29.0	29.1	40.0	25.4	27.1
1-Butene	27.9	39.3	41.0	0.071	0.064	0.061	14.3	10.8	10.7	34.5	11.3	11.6
Water	62.7	83.1	73.4	0.103	0.105	0.116	111.1	112.4	112.8	103.5	114.2	113.2
Ammonia	78.1	70.9	80.9	0.237	0.243	0.268	77.4	79.6	79.6	67.0	77.9	78.1
Average	77.6	86.1	106.1	0.152	0.155	0.202	37.9	35.3	34.4	55.1	42.9	45.5

TABLE 2b (continued)

Compound	ΔU (cal mol^{-1})			f/P			T_r range	P_r range	N	Ref.[a]
	SRK	PR	LM	SRK	PR	LM				
Methane	18.2	13.8	21.6	0.0104	0.0337	0.0381	1.007–7.343	0.022–21.83	272	5
Ethane	47.6	55.4	69.4	0.0135	0.0156	0.0186	1.002–1.768	0.021–10.37	108	6
Propane	53.2	65.5	164.5	0.0264	0.0186	0.0225	1.000–1.892	0.024–16.66	180	5
n-Butane	66.9	77.7	170.3	0.0242	0.0153	0.0168	1.002–1.411	0.027–18.68	69	7
i-Butane	60.9	74.9	97.1	0.0180	0.0161	0.0178	1.005–1.715	0.028–11.11	165	5
n-Pentane	165.8	158.3	274.2	0.0284	0.0226	0.0249	1.001–1.491	0.030–21.05	144	5
i-Pentane	77.4	67.1	78.3	0.0234	0.0096	0.0112	1.021–1.738	0.030–8.990	160	5
Neopentane	50.8	56.0	86.0	0.0135	0.0204	0.0228	1.014–1.614	0.032–11.10	153	5
n-Hexane	215.1	214.3	193.4	0.0315	0.0135	0.0157	1.006–1.159	0.033–1.365	174	8
n-Heptane	106.2	113.5	105.2	0.0426	0.0179	0.0170	1.037–1.851	0.037–18.28	156	5
n-Octane	141.5	148.7	153.1	0.0521	0.0243	0.0237	1.020–1.758	0.041–20.14	143	5
Benzene	35.0	40.4	36.3	0.0062	0.0065	0.0071	1.031–1.777	0.021–2.027	132	5
Carbon dioxide	73.0	78.1	93.3	0.0135	0.0133	0.0166	1.022–4.492	0.014–2.804	120	8
Sulphur dioxide	96.5	102.8	103.6	0.0301	0.0324	0.0326	1.019–1.212	0.013–3.936	180	8
Methanol	93.0	99.5	109.5	0.0187	0.0136	0.0142	1.013–1.949	0.013–6.907	208	5
Ethanol	94.4	101.9	144.3	0.0271	0.0173	0.0218	1.012–1.946	0.017–8.147	182	5
1-Propanol	116.6	125.3	177.0	0.0310	0.0185	0.0239	1.043–1.862	0.020–9.878	169	5
Acetylene	76.7	78.6	50.0	0.0207	0.0056	0.0077	1.001–1.034	0.016–1.435	63	8
Propylene	30.4	33.1	40.8	0.0091	0.0076	0.0097	1.020–3.745	0.022–4.476	130	8
1-Butene	34.9	37.1	37.9	0.0203	0.0080	0.0083	1.049–2.383	0.025–12.44	195	5
Water	74.9	81.8	69.3	0.0055	0.0053	0.0048	1.038–1.768	0.005–1.714	194	8
Ammonia	64.3	65.8	75.6	0.0101	0.0069	0.0076	1.041–1.452	0.009–3.056	120	8
Average	81.5	85.9	106.9	0.0217	0.0156	0.0174	Total number of data points = 34.17			

[a] $P-V-T$, departure function and fugacity coefficient data are taken from the same source.

physical constants used as input data for all calculations have been listed in Table 1.

Region III—Supercritical

In the supercritical region predictions of P–V–T, five departure functions (ΔH, ΔS, ΔA, ΔG, ΔU) and the fugacity coefficient obtained from the SRK, PR and LM (this work) equations have been tested against the experimental data. The data sources for all the compounds are listed in

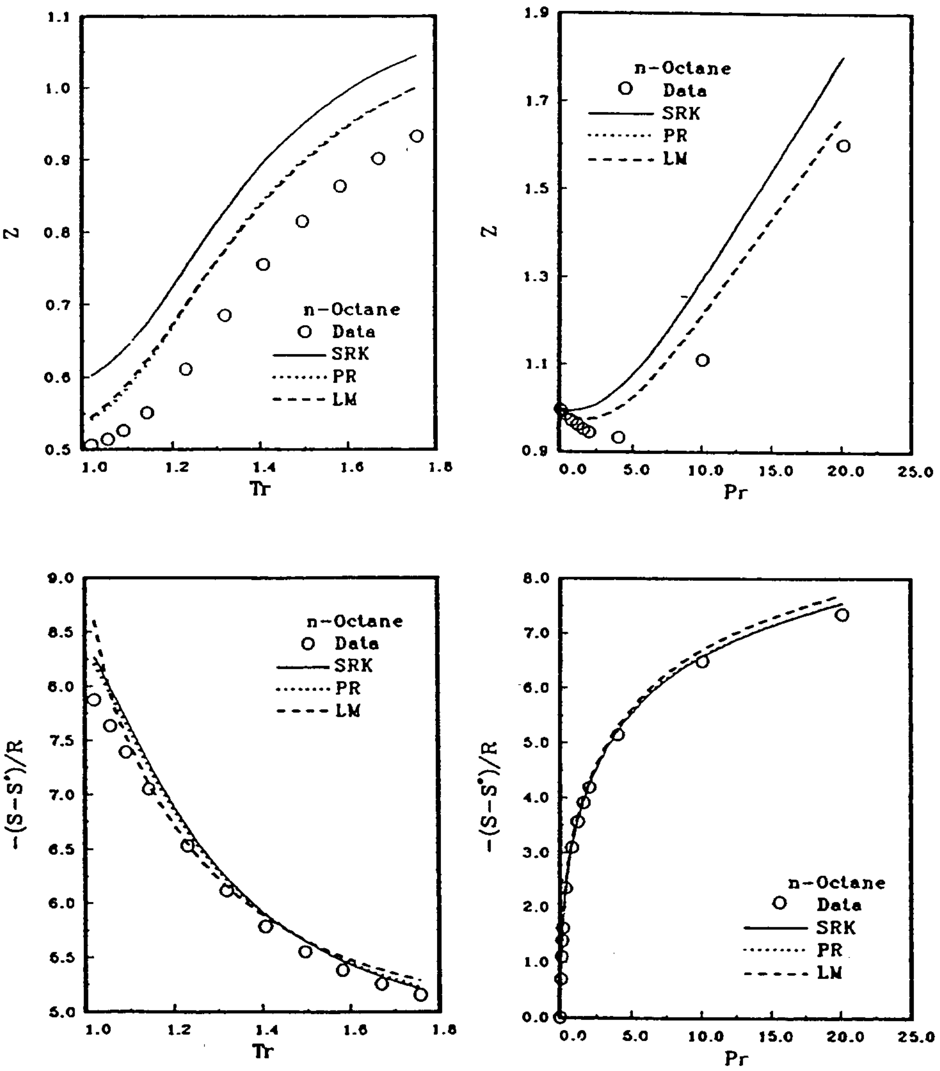

Fig. 2. Region III. Compressibility factors and reduced entropy departure functions of n-octane versus reduced temperature ($P_r = 4.03$) and reduced pressure ($T_r = 1.76$).

TABLE 3a

Comparison of prediction errors: Region IV—compressed liquid

Compound	RMS % Error									T_r range	P_r range	N	Ref. [a]
	P			T			V						
	SRK	PR	LM	SRK	PR	LM	SRK	PR	LM				
Methane	179	1144	1174	2.792	18.29	18.47	3.610	9.831	10.01	0.525–0.944	0.216–0.862	86	9,10
Ethane	718	876	904	6.965	10.47	10.42	10.93	6.410	6.125	0.519–0.994	0.551–0.981	48	9,11
Propane	1104	637	643	9.893	7.171	7.095	8.831	4.943	4.898	0.622–0.919	0.211–0.940	84	9,10
n-Butane	698	171	173	10.17	3.072	3.050	12.33	3.177	3.056	0.690–0.925	0.527–0.790	16	9,10
i-Butane	468	172	172	8.177	3.545	3.509	11.49	3.464	3.374	0.718–0.939	0.548–0.822	13	9,10
n-Pentane	2139	333	344	16.09	3.624	3.606	10.82	2.292	2.283	0.624–0.837	0.297–0.891	24	9,10
n-Hexane	2001	132	123	16.36	1.758	1.612	14.20	2.951	2.280	0.676–0.951	0.330–0.990	23	9,10
n-Heptane	70070	1555	1417	36.30	2.079	1.803	13.70	1.537	1.267	0.555–0.926	0.037–0.731	49	5
n-Octane	–	4639	4583	45.46	6.204	5.894	16.69	3.793	3.430	0.563–0.949	0.041–0.806	54	5
Benzene	28112	5722	5932	20.24	7.268	7.207	9.761	3.637	3.593	0.551–0.942	0.021–0.811	53	5
Carbon dioxide	722	139	128	8.083	1.891	1.771	12.43	3.184	2.962	0.799–0.964	0.206–0.824	23	9,12
Methanol	–	–	–	–	–	–	37.36	21.43	21.24	0.702–0.857	0.038–0.628	27	5
Ethanol	97345	10358	10446	39.48	10.46	10.45	23.81	9.929	9.324	0.701–0.973	0.033–0.815	37	5
1-Propanol	64189	4181	4248	31.85	5.078	5.128	18.85	5.832	5.991	0.670–0.968	0.020–0.786	41	5
1-Butene	15773	4942	5383	16.15	8.418	8.617	8.895	4.519	4.643	0.572–0.953	0.025–0.746	38	5
Water	–	–	–	–	–	–	37.83	22.18	21.74	0.515–0.963	0.203–0.904	118	9,13
Nitrogen	130	485	492	2.872	8.757	8.936	7.070	8.709	8.780	0.715–0.953	0.209–0.896	17	9,12
Ammonia	5505	1346	1353	32.62	12.95	12.95	30.86	15.73	15.52	0.764–0.962	0.269–0.898	54	9,12
Neon	670	1217	1127	9.881	24.06	23.27	4.872	15.04	14.42	0.563–0.901	0.226–0.942	20	9,10
Argon	152	918	929	2.435	16.54	16.67	3.978	10.74	10.85	0.563–0.961	0.204–0.919	53	9,10
Average	> 100	> 100	> 100	17.55	8.42	8.36	14.92	7.97	7.79				

[a] $P-V-T$, departure function and fugacity coefficient data are taken from the same source.

TABLE 3b

Comparison of prediction errors: Region IV–compressed liquid

Compound	Average absolute deviation (AAD)											
	ΔH (cal mol^{-1})			ΔS (cal mol^{-1} K^{-1})			ΔA (cal mol^{-1})			ΔG (cal mol^{-1})		
	SRK	PR	LM	SRK	PR	LM	SRK	PR	LM	SRK	PR	LM
Methane	42.6	10.3	37.7	–	–	–	–	–	–	–	–	–
Ethane	89.0	60.3	98.7	–	–	–	–	–	–	–	–	–
Propane	77.8	37.5	81.8	–	–	–	–	–	–	–	–	–
n-Butane	68.2	45.7	91.4	–	–	–	–	–	–	–	–	–
i-Butane	68.4	47.4	81.9	–	–	–	–	–	–	–	–	–
n-Pentane	52.3	31.9	88.7	–	–	–	–	–	–	–	–	–
n-Hexane	85.9	56.5	91.5	–	–	–	–	–	–	–	–	–
n-Heptane	186.5	238.2	48.8	0.531	0.739	0.273	71.1	65.2	68.1	66.3	65.5	67.8
n-Octane	214.0	233.8	69.5	0.511	0.670	0.312	101.4	93.4	97.9	94.6	95.1	96.5
Benzene	122.1	146.3	59.7	0.405	0.447	0.138	65.0	35.7	40.3	60.8	34.9	41.2
Carbon dioxide	49.9	38.6	61.9	–	–	–	–	–	–	–	–	–
Methanol	510.0	629.2	887.6	1.325	1.649	2.305	39.3	44.7	64.7	35.8	46.7	62.8
Ethanol	132.0	208.2	300.3	0.346	0.612	0.871	58.6	53.4	62.7	47.6	58.0	58.6
1-Propanol	159.7	229.2	32.8	0.413	0.657	0.198	83.2	75.5	62.0	74.0	78.4	59.0
1-Butene	93.6	158.0	73.5	0.342	0.583	0.247	11.5	18.6	20.9	9.6	18.4	21.8
Water	76.4	164.3	408.7	–	–	–	–	–	–	–	–	–
Nitrogen	25.9	14.5	14.6	–	–	–	–	–	–	–	–	–
Ammonia	71.1	51.9	87.4	–	–	–	–	–	–	–	–	–
Neon	9.5	2.5	17.4	–	–	–	–	–	–	–	–	–
Argon	28.1	10.5	14.8	–	–	–	–	–	–	–	–	–
Average	108.2	120.7	132.4	0.553	0.765	0.621	61.4	56.7	59.5	55.5	55.2	58.2

TABLE 3b (continued)

Compound	ΔU (cal mol^{-1})			f/P						
	SRK	PR	LM	SRK	PR	LM	T_r range	P_r range	N	Ref. [a]
Methane	42.8	9.6	36.0	–	–	–	0.525–0.944	0.216–0.862	86	9,10
Ethane	86.6	58.5	96.9	–	–	–	0.519–0.994	0.551–0.981	48	9,11
Propane	80.1	35.7	80.1	–	–	–	0.622–0.919	0.211–0.940	84	9,10
n-Butane	69.4	44.8	90.5	–	–	–	0.690–0.925	0.527–0.790	16	9,10
i-Butane	66.7	45.5	80.7	–	–	–	0.718–0.939	0.548–0.822	13	9,10
n-Pentane	58.8	31.8	88.2	–	–	–	0.624–0.837	0.297–0.891	24	9,10
n-Hexane	87.5	55.1	90.9	–	–	–	0.676–0.951	0.330–0.990	23	9,10
n-Heptane	188.7	238.6	49.1	0.0222	0.0242	0.0238	0.555–0.926	0.037–0.731	49	5
n-Octane	218.1	234.7	70.2	0.0282	0.0308	0.0316	0.563–0.949	0.041–0.806	54	5
Benzene	124.4	146.6	59.1	0.1336	0.0153	0.0156	0.551–0.942	0.021–0.811	53	5
Carbon dioxide	49.3	37.5	61.4	–	–	–	0.799–0.964	0.206–0.824	23	9,12
Methanol	497.8	622.1	880.7	0.0159	0.0203	0.0285	0.702–0.857	0.038–0.628	27	5
Ethanol	135.9	207.8	298.7	0.0190	0.0223	0.0255	0.701–0.973	0.033–0.815	37	5
1-Propanol	164.6	231.1	30.2	0.0300	0.0315	0.0248	0.670–0.968	0.020–0.786	41	5
1-Butene	93.2	158.6	72.8	0.0038	0.0083	0.0100	0.572–0.953	0.025–0.746	38	5
Water	76.8	157.1	395.7	–	–	–	0.515–0.963	0.203–0.904	118	9,13
Nitrogen	25.6	13.1	13.4	–	–	–	0.715–0.953	0.209–0.896	17	9,12
Ammonia	72.9	51.4	78.9	–	–	–	0.764–0.962	0.269–0.898	54	9,12
Neon	9.3	2.3	18.3	–	–	–	0.563–0.901	0.226–0.942	20	9,10
Argon	27.8	10.4	14.6	–	–	–	0.563–0.961	0.204–0.919	53	9,10
Average	108.8	119.6	130.3	0.0361	0.0218	0.0228				

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[a] P–V–T, departure function and fugacity coefficient data are taken from the same source.

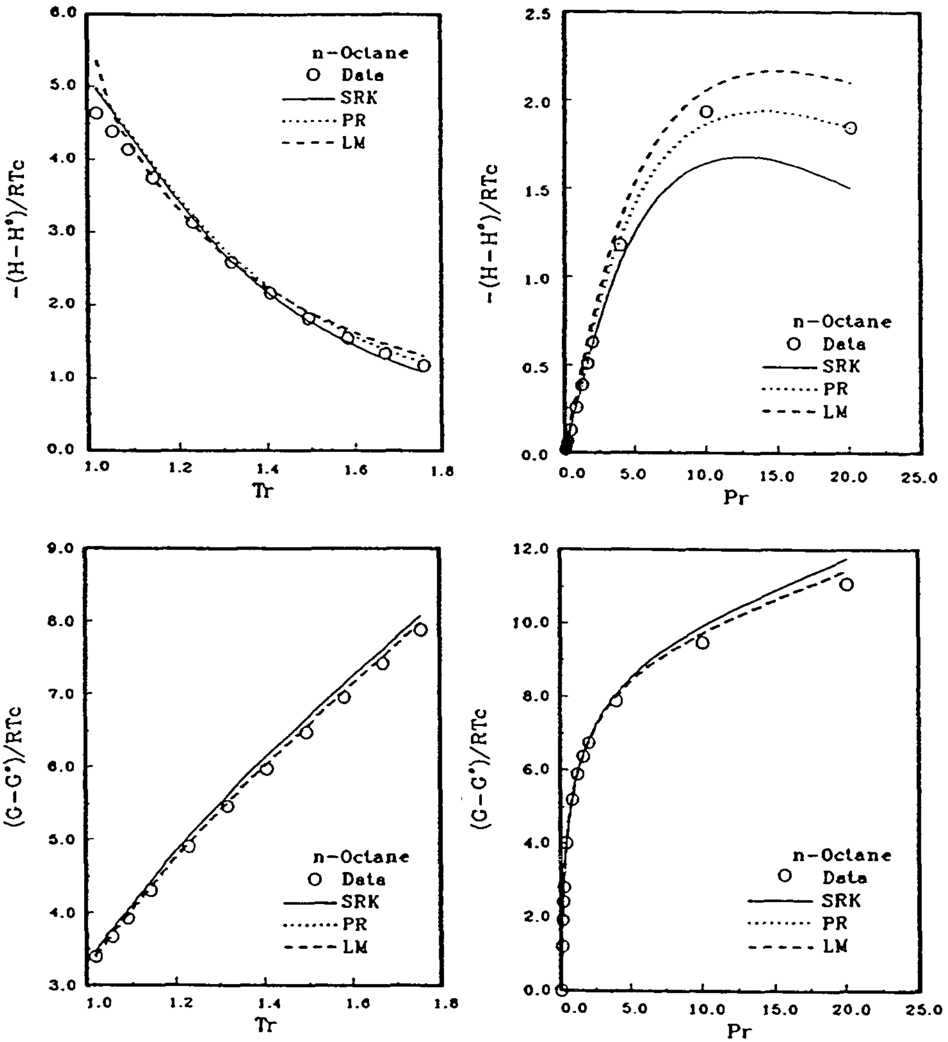

Fig. 3. Region III. Reduced enthalpy and reduced Gibbs energy departure functions of *n*-octane versus reduced temperature ($P_r = 4.03$) and reduced pressure ($T_r = 1.76$).

Tables 2a and 2b. The results of the P–V–T predictions of these equations are given in Tables 2a and 2b. For pressure prediction, the PR and LM equations are similar in accuracy. The overall average RMS % error from the SRK equation is about double that of the PR or LM equation. For the temperature prediction, all three equations are about the same in accuracy. For volume prediction, the PR and LM equations are again similar in accuracy for most compounds. However, in terms of the overall average RMS % error, the PR equation yields the lowest. In many cases, the error from the SRK equation is almost twice that of the PR or LM equation. Similar results were also obtained by Lielmezs and Mak [1] in the satura-

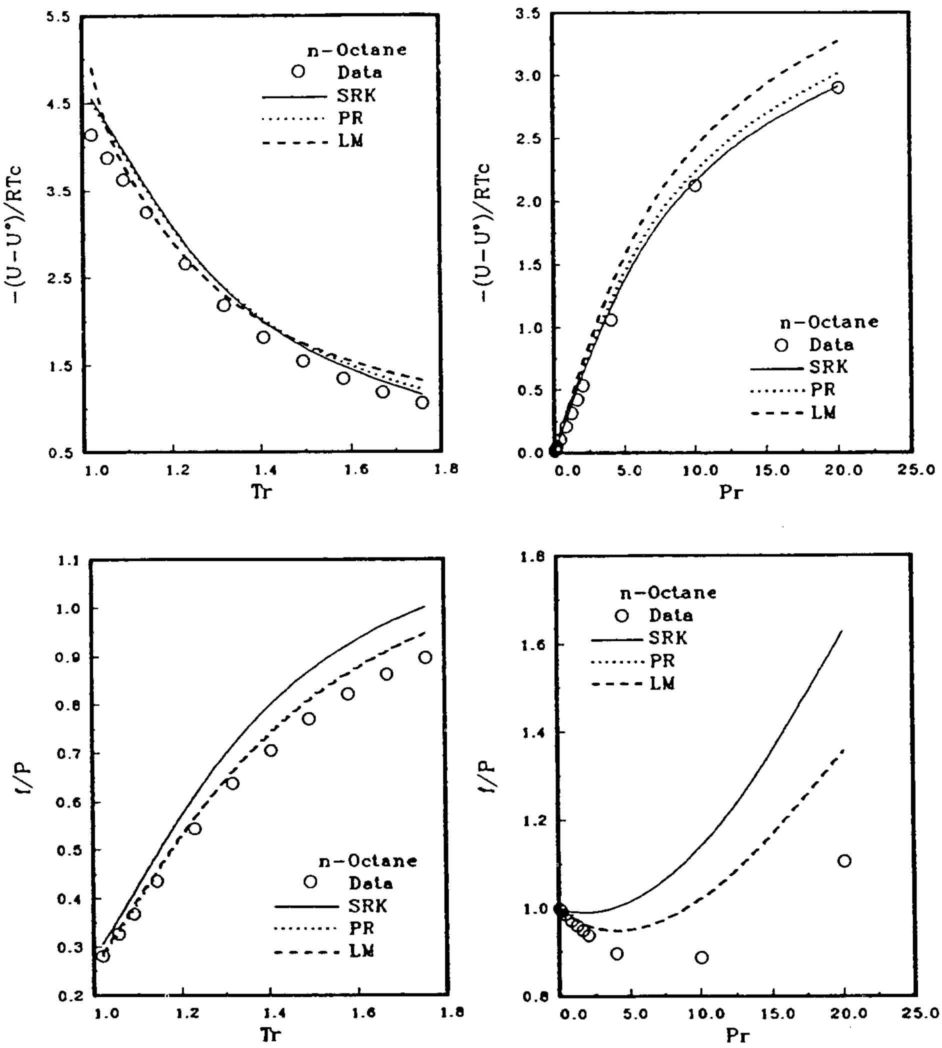

Fig. 4. Region III. Reduced internal energy departure functions and fugacity coefficients of *n*-octane versus reduced temperature ($P_r = 4.03$) and reduced pressure ($T_r = 1.76$).

tion region. As a typical example, Fig. 2 presents plots of compressibility versus reduced temperature and reduced pressure for *n*-octane.

The results for the five departure functions (ΔH, ΔS, ΔA, ΔG, ΔU) are summarized in Table 2b. In terms of the overall deviation (AAD), the SRK and PR equations are similar for the ΔH, ΔS and ΔU departure functions. As already noted by Lielmezs and Mak [1], the LM equation is poor near the critical temperature because the derivative of the α-function (eqn. (3), Lielmezs and Mak [1]) with respect to temperature approaches infinity as the temperature approaches the critical value. However, above $T = 1.05$, the predictions from the LM equation are similar to those of the SRK and PR equations (Tables 2a and 2b, Figs. 2–4). For ΔA and ΔG departure

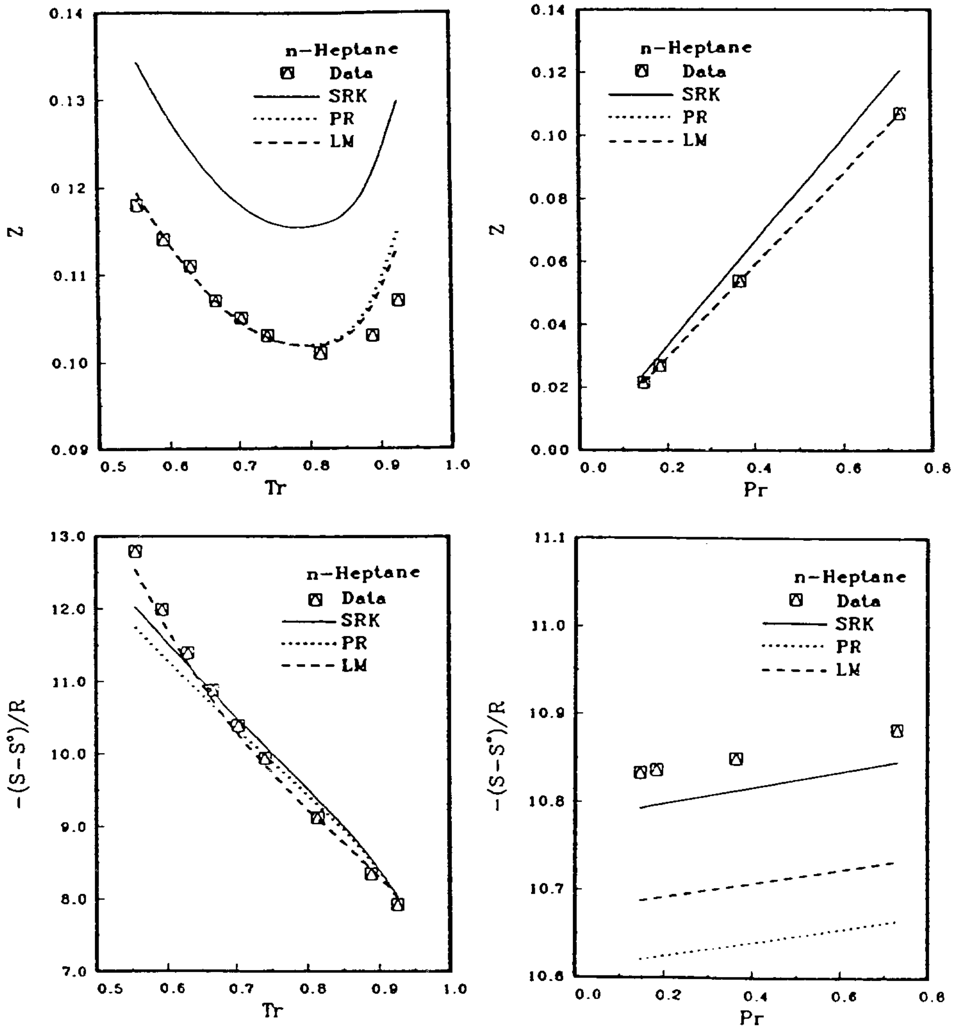

Fig. 5. Region IV. Compressibility factors and reduced entropy departure functions of *n*-heptane versus reduced temperature ($P_r = 0.73$) and reduced pressure ($T_r = 0.67$).

functions, error cancellation near the critical point results in similar accuracy for all three equations considered (Table 2b, Fig. 3). For the fugacity coefficient calculation, the SRK equation shows the best accuracy (Table 2b, Fig. 4). It is of interest to note that although the α-functions of the PR and LM equations are so different (for a detailed discussion see Lielmezs and Mak [1]), the predictive accuracy of these two equations is similar for a number of compounds (Tables 2a and 2b).

Region IV—compressed liquid

In the compressed liquid region predictions of P–V–T, the five departure functions (ΔH, ΔS, ΔA, ΔG, ΔU) and fugacity coefficient obtained

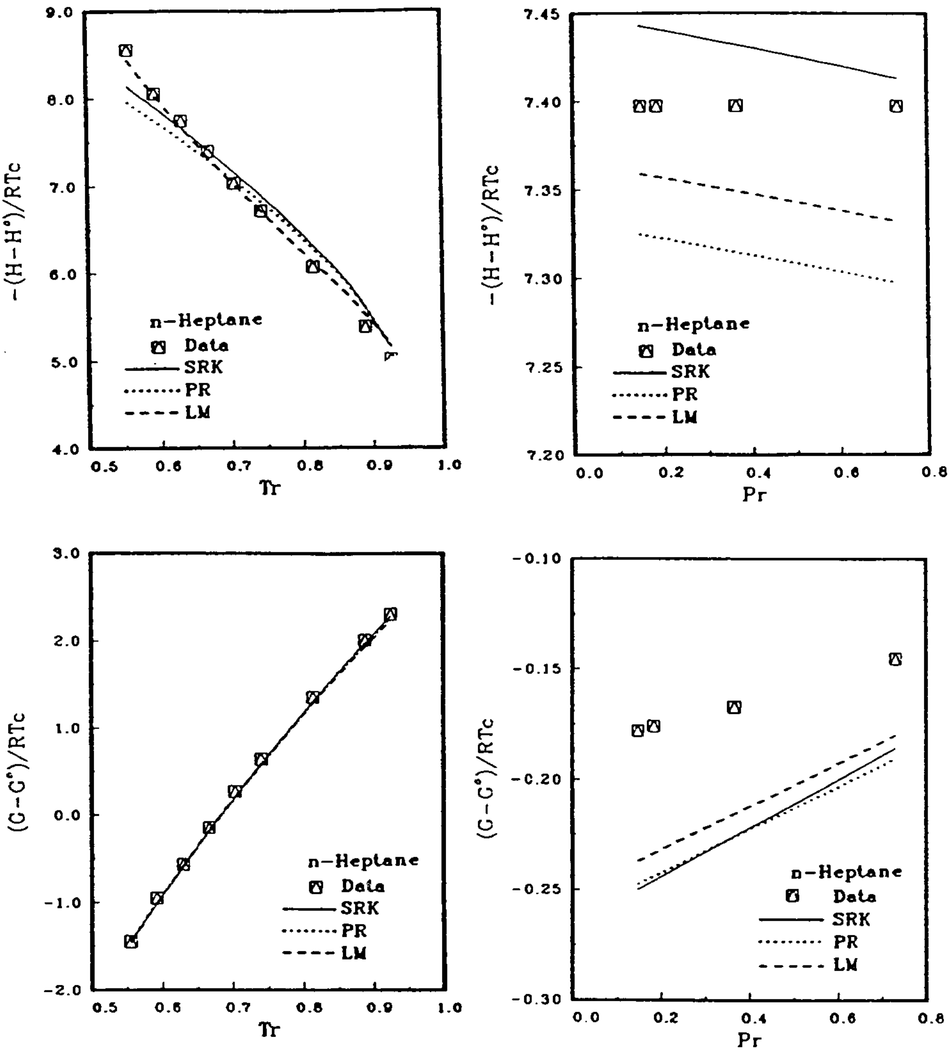

Fig. 6. Region IV. Reduced enthalpy and reduced Gibbs energy departure functions of *n*-heptane versus reduced temperature ($P_r = 0.73$) and reduced pressure ($T_r = 0.67$).

by means of the SRK, PR and LM (this work) equations have been compared with experimental data. The number of compounds studied, however, has been limited due to the lack of experimental data, especially data on departure functions. The experimental data sources are listed in Tables 3a and 3b. The RMS % errors of the *P–V–T* prediction by the SRK, PR and LM equations are given in Tables 3a and 3b. For pressure prediction, all three equations yield very large errors. For temperature estimation, the magnitude of errors from the PR and LM equations is the same in all cases while the SRK equation gives substantially larger errors. In terms of an overall average RMS % error, the errors stemming from PR

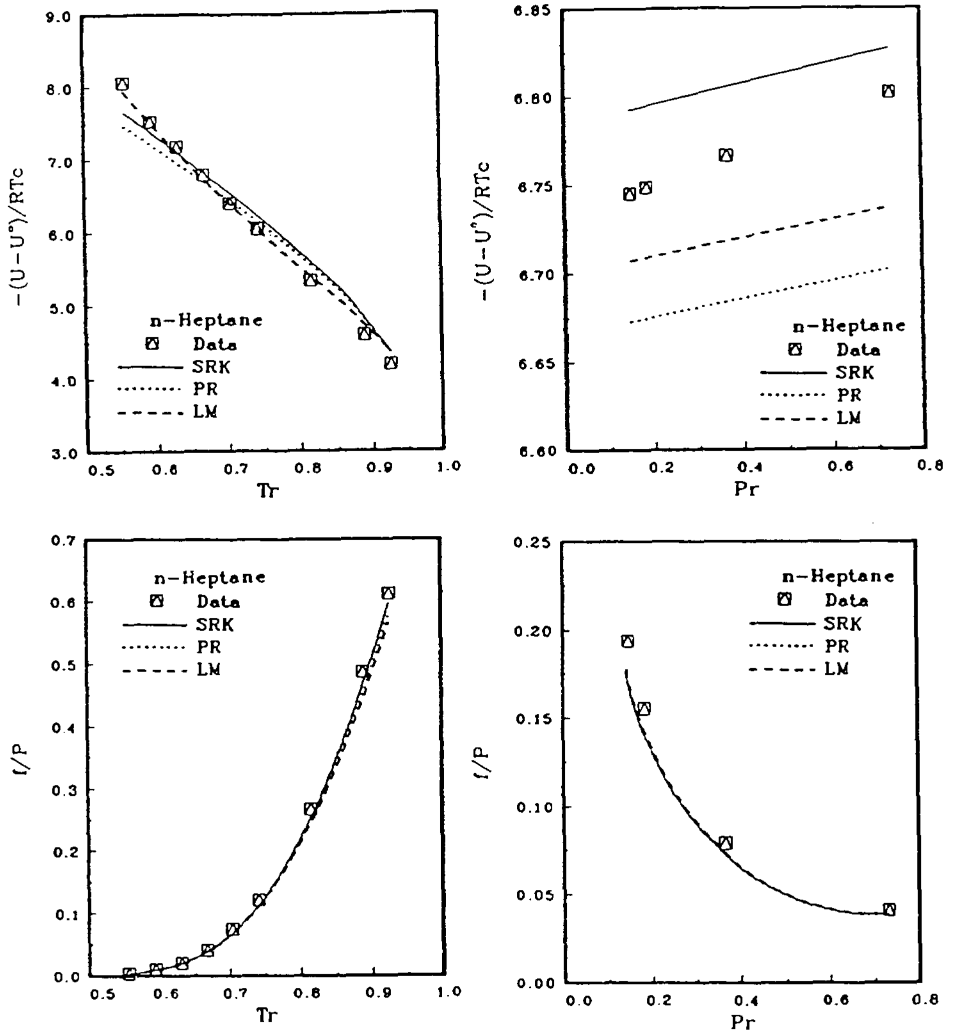

Fig. 7. Region IV. Reduced internal energy departure functions and fugacity coefficients of *n*-heptane versus reduced temperature ($P_r = 4.03$) and reduced pressure ($T_r = 1.76$).

and LM equations are about half that of the SRK equation (Table 3a). Similar conclusions are also drawn for the volume prediction (Table 3a). As a typical example of error distribution patterns, Fig. 5 presents the compressibility factor for *n*-heptane plotted against the reduced temperature and pressure.

The results of the five departure functions (ΔH, ΔS, ΔA, ΔG, ΔU) are given in Table 3b. As already noted, experimental data on departure functions in this region are limited. The TRC data book [5] contains enthalpy and entropy departure function data for seven of the compounds tested in this work (Table 3b).

The use of Lu et al.'s correlation [9] for estimating the enthalpy departure function for compressed liquids enabled the testing of the enthalpy and internal energy departure functions over a limited reduced temperature range [1] for an additional thirteen compounds (Table 3b). The results of the comparison for the five departure functions and fugacity coefficients are listed in Table 3b. Figures 5–7 give plots of the five departure functions and the fugacity coefficient against the reduced temperature and pressure for *n*-heptane. The overall results obtained (Tables 3a and 3b, Figs. 5–7) show that for the compressed liquid region none of the three equations is adequate for predicting the considered thermodynamic properties. The accuracy of the PR and LM equations is similar for volume and temperature prediction. For pressure predictions all three equations are poor. For departure functions and fugacity coefficient prediction, all three equations are similar.

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